Catalytic Processes in Biorefinery

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Abstract

The esterification reaction with methanol of oils or fats containing free fatty acids (FFA) can be performed for a direct biodiesel production. This is a pre-treatment step, requiring an acid catalyst, in the framework of a conventional transesterification process, this last promoted by an alkaline homogeneous catalyst (NaOH, KOH or related methoxides). The esterification of FFAs with methanol is currently carried out in the presence of strong Brønsted acid catalysts such as sulfuric acid or p-toluenesulfonic acid [1,2]. When the acid catalyst is homogeneous, before starting the second transesterification step we need to neutralize the acid catalyst.

For this reason heterogeneous catalysts like sulfonic resin or acid oxides seem more attractive [3,4]. However, for the same esterification reaction, other authors reported the use of heterogeneous catalysts [5-6]. A variety of unsaturated fatty acids, such as oleic, linoleic, erucic, ricinoleic, hydroxystearic and coriolic acid, were used for this purpose.

In this work, we have studied the performances of some different heterogeneous catalysts in promoting the esterification of oleic acid with glycerol. In particular, we have tested the behaviour of respectively: Amberlyst-15, Naftion, and new type of temperature resistant acid resins (200-220°C), Sulfonated Multiblock Copolymers Syndiotactic Polystyrene-co-1,4-cis-Polybutadiene [7,8].

These acid resins have shown very interesting performances in the described reaction, in comparison with both the other heterogeneous catalysts and sulphuric acid. Moreover, they can be used at temperatures much higher than the conventional commercially available sulphonic resins. This has a beneficial effect on the reaction rate and on the possibility of shifting the equilibrium by continuously removing produced water from the reaction environment.

The same catalysts are tested also in other esterification reaction to obtain lubricant bases. In the last years the biolubricants have arouse a great interest in the scientific background and represent an alternative to the petrochemical lubricants thanks to their properties like the high viscosity index, the high flash point and the low friction coefficient [9,10]. Another aspect is the reduction of environmental impact of biolubricants, in fact, they are more degradable, less toxic and so less polluting than mineral lubricants.

In this work biolubricants synthesis from vegetable oils through esterification reaction has been studied. In the experimental tests the vegetable oils are esterificated in the presence of acid catalysts. In particular tungstic acid on silica (synthesized through impregnation) and Sulfonated Multiblock Copolymers Syndiotactic Polystyrene-co-1,4-cis-Polybutadiene have been used. The purpose is to verify the catalytic activity and reuse possibility the catalysts.

The results obtained, both in the case of the synthesis of glycerides both in the case of the synthesis of lubricants, are encouraging.

References


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